Homogeneous selective peroxidic oxidation of hydrocarbons using an oxovanadium based catalyst

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Abstract

Some representative benzylic, aromatic, heterocyclic, carbocyclic and aliphatic hydrocarbons are selectively oxidized in acetonitrile solution medium to their respective aldehydes, phenols, oxides, alcohols and ketones without any over-oxidation to carboxylic acids, in the homogeneous mode using an oxovanadium(V) hydroxamate as catalyst and H_2O_2 as terminal oxidant. The yield percentage is quite good and the turnover number in each case is highly satisfactory.
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1. Introduction

Homogeneous metal catalyzed oxidation of organic substrates with hydrogen peroxide as a terminal oxidant is rapidly gaining momentum as a green, cost-effective and viable alternative to the hazardous stoichiometric oxidation using nitric acid, hypochlorite, permanganate and chromate as reagents [1]. Catalytically achieved hydrocarbon oxidation by generating their alcoholic, phenolic, carbonyl or carboxylic acid functions is an extremely fascinating research area [2–6] since, with the functionalities generated, it is possible to plan a wide variety of organic synthesis for laboratory as well as industrial use. In this respect more recently we have seen that transition metal containing catalysts in combination with various oxidizing agents can convert a wide variety of hydrocarbons including lower alkanes (only two such reports though, [6] and [7(g)]) into the corresponding oxidized products [7]. Concerning the specific catalysts only two reports appeared in the literature [8,9] on the oxidation of alkyl benzenes using oxoperoxo molybdenum (VI) complexes as catalyst and H_2O_2 as oxidant in aerobic or dioxygenic atmosphere. On the contrary, vanadium compounds have been widely used as catalyst in peroxidic as well as dioxygenic oxidation of hydrocarbons [2,5,10], but so far yields and TON obtained are not very remarkable. However, high reaction yields were obtained by Barnhard and Huges by using vanadium complexes as catalyst, but the assistance of a reducing agent, namely, substituted hydrocarbons, in high amount was necessary [11], which made the process less cost-effective.

In the present paper we report a high yield, high TON conversion of some typical and representative aromatic (benzene, toluene, naphthalene), heterocyclic (pyridine), carbocyclic (cyclohexane) and aliphatic (*n*-heptane) hydrocarbons (many of which are the by-products of petroleum cracking and coal tar distillation) using $[V(O)(Cl)(PBHA)_2]$ **1** (PBHA$^-$ = *N*-phenyl benzohydroxamate) as catalyst and H_2O_2 as oxidant in acetonitrile medium. It is well known that bacteria and algae very often produce low molecular weight chelators (siderophores) which are capable of sequestering metal ions and facilitate the transport of these nutrients into the cell [12]. Two very important classes of siderophores are catecholate and hydroxamate based metal complexes [13]. In view of the isolation of vanadium

bromoperoxidase from algae and bacteria, we thought it worthwhile to use hydroxamic acid as ligand so as to get oxovanadium hydroxamate as a catalyst. Pande and Tandon [14] first prepared **1**, but we simplified the method of preparation and the simplified version is reported here. We also report here the X-ray crystal structure of the catalyst **1** insofar as, discussion regarding the actual mechanistic aspect of the substrate–catalyst–oxidant reaction, will be more meaningful when we know with certainty, the structure of each component. Notably, there exist two references [15,16] in the literature where hydroxamate ligands have been used as catalyst: (i) Oxoperoxo molybdenum (VI)–PBHA complex was used in the oxidation of alcohols to carbonyl compounds and (ii) a preliminary report appeared on the use of chiral hydroxamic acid as ligands for the vanadium catalyzed asymmetric epoxidation of allylic alcohols. In both the cases *t*-butyl hydro peroxide was used as terminal oxidant, TON was low and in the case of epoxidation, conversion required days.

2. Experimental

2.1. Physical measurements

The IR spectra were recorded as KBr pellets on a Perkin–Elmer 597 IR spectrophotometer (4000–200 cm^{-1}) and Electronic spectra on a Hitachi U-3410 UV/VIS/NIR spectrophotometer. A Systronics (India) model 335 digital conductivity bridge with a bottle type cell was used to determine the conductance values of the acetonitrile solution of the complex **1** at 25 °C using a thermostatic arrangement. A SUNVIC (UK) apparatus was used to measure melting point of the organic substrates as well as of their oxidized products. The magnetic data were recorded using Gouy method using Hg [Co(SCN)$_4$] as a standard. Elemental analysis was performed with the help of a Perkin–Elmer 240C elemental analyzer, and molybdenum was estimated gravimetrically as its 8-quinolinolate [17]. GLC measurements were done in an Agilent model 6890 gas chromatograph using HP-1 and INNOWAX capillary column in FID mode with dinitrogen as carrier gas maintaining the oven temperature at 35 °C for 5 min and then programmed to 140 °C at 10 °C/min. Some routine GC run was done with the HP model 5880 gas chromatograph using OV–101 packed column in the similar way.

2.2. Materials

Ammonium metavanadate, dinitrophenyl hydrazine and zinc dust were of extrapure variety and obtained from Loba Chemie (India). Sodium bicarbonate, benzyl alcohol and phenol were the products of Sisco Research Laboratories (SRL, India) and were directly used. Nitrobenzene of Laboratory Reagent grade was obtained from B.D.H. (India) benzoyl chloride and thionyl chloride of synthetic reagent grade were obtained from Ranbaxy (India). Ethanol (95%) was

obtained from Bengal Chemical and Pharmaceutical Works (Calcutta) and was lime-distilled before use. All other chemicals needed were obtained from E. Merck (India). Acetonitrile, dichloromethane and acetone were further purified by literature method [18] for physico-chemical studies. Ultra high pure grade dioxygen, dihydrogen, zero air and dinitrogen gas used for chromatographic analysis were obtained from Indian Refrigeration Stores, Calcutta. Triply distilled (all glass) water was used whenever necessary. The ligands *N*-phenyl benzohydroxamic acid was synthesized following the method described in the literature [19] and characterized by elemental analysis, melting point and IR data. All the solvents used for chromatographic analysis were either of HPLC, spectroscopic, or GR grade and in all cases their purity was confirmed by GC analysis before use.
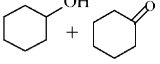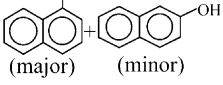
2.3. Preparation of the complex [V(O)(Cl) (PBHA)$_2$]

An aqueous (15 ml) solution of NH$_4$VO$_3$ (1.17 g, 10 mmol) was treated with 6 ml of concentrated HCl and stirred when a yellow solution was obtained. This solution was added to an ethanolic (30 ml) solution of PBHAH (4.32 g, 20.3 mmol) with stirring. The stirring was continued for another 1 h when a deep violet precipitate was obtained. The s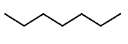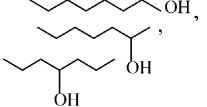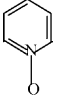olid was filtered off and washed with distilled water and 1:1 ethanol and vacuum dried. Yields: 3.37 g (65%). The compound is soluble in acetone, acetonitrile, dichloromethane, methanol, ethanol, nitromethane, toluene and benzene but insoluble in hexane and light petroleum. The crude compound was crystallized by slow diffusion of *n*-hexane through dichloromethane solution of the compound when shinning deep violet crystals appeared. Anal. Calc. For C$_{26}$H$_{20}$N$_2$O$_5$ClV, C, 59.28; H, 3.83; N, 5.32; Cl, 6.73 and V, 9.67%. Found, C, 58.87; H, 3.75; N, 5.47; Cl, 7.01 and V, 10.12%. IR (KBr disc; cm^{-1}) 3040 (w), 1600 (m), 1585 (m), 1530 (s) and 1500 (s) [ν (C=O)], 1470 (s) [ν (C–N)], 1455 (m), 1430 (s), 1380 (s), 1270 (m), 1180 (w), 1160 (w), 1140 (m), 1070 (w), 1040 (w), 1015 (m), 1000 (w), 970 (s) [ν (V=O)], 937 (m), 920 (w), 770 (s), 720 (m), 695 (s), 665 (m), 645 (m), 620 (w), 580 (m), 560 (m), 500 (m), 460 (m), 380 (w), 360 (m) [ν (V–Cl)]. UV-Vis (λ, nm): 529 ($\in$= 3550 M^{-1} cm^{-1}), 270 (sh), 224 (sh).

2.4. X-ray crystallography

Crystal data: C$_{26}$H$_{20}$O$_5$N$_2$ClV, M = 526.83, monoclinic, space group $P2_1/c$ (no. 14) a = 12.127(1), b = 15.666(1), c = 18.055(1) Å, β = 131.124(4)°, V = 2583.9(3) Å^3, Z = 4, D_c = 1.354 g/cm^3, μ(Mo-Kα) = 0.52 mm^{-1}, Mo-Kα (λ = 0.71073 Å). The structure was solved by direct methods of SHELXS97 [20] and refined by full-matrix least-square (on F^2) with anisotropic thermal parameters to all non-hydrogen atoms. The final residuals for 3144 reflections with |F$_o$|≥4σ(|F$_o$|) were R_1 = 0.0779, wR_2 = 0.2186, GooF = 0.978 and number of refined parameters were 316.

Table 1
Details of catalytic oxidation of the hydrocarbons (as well as pyridine) in refluxing CH_3CN^a using $H_2O_2{}^b$ as oxidant and **1** as catalyst[c]

Entry	Substrate	Product	% Yield[d]	% Selectivity[e]	Turnover number
I	(toluene, CH_3)	(benzaldehyde, CHO)	70	100	72
II	(benzene)	(phenol, OH)	75	100	172
III	(cyclohexane)	(cyclohexanol, OH) + (cyclohexanone, O)	66 (7:6.2)	53, 47	270, 260
IV	(naphthalene)	(1-naphthol, OH) (major) + (2-naphthol, OH) (minor)	83.5 (7:5)	59, 41	27, 18
V	(n-octane)	(OH), (OH), (OH)	79.2 (1:1.03:1.05)	32, 33, 34	59, 60, 62
VI	(pyridine)	(pyridine N-oxide, O)	96	100	517

[a] Time of reflux: 5 h.
[b] Concentration of H_2O_2 = 53 mmol.
[c] Concentration of catalyst = 0.023 mmol.
[d] Based on substrate concentration.
[e] Turnover number is defined here as the ratio of the of moles of product obtained to the moles of catalyst used. The mole ratio of substrate:catalyst for (i) and (iv) 100:1, for (ii), (iii) and (v) 200:1 and for (vi) 600:1. This variation in the mole ratio was felt necessary to optimize the yield percentage.

2.5. Experimental set up for catalytic oxidation

A mixture of complex **1** (the catalyst) (0.098 g; 0.188 mmol), a representative substrate, namely toluene (2 ml; 18.8 mmol; for other cases see Table 1), was dissolved in 10 ml CH_3CN solvent and the resulting solution was taken in a 100 ml capacity Parr type hydrogenation apparatus. To the above solution was then added 3 ml of 30% H_2O_2 (26.5 mmol) when the resulting solution turned yellow. The assembly was then plunged in water taken in a suitable plastic container, to be assured that the system was air-tight. Another 3 ml of H_2O_2 was added intermittently with 0.5 ml at a time until 30 min before the reaction subsides. The solution was then heated (oil bath) to reflux (85 °C) up to 5 h, but after every one-hour interval 0.1 ml of the refluxing solution was taken out with a long needle syringe through the septum of the apparatus. The withdrawn solution was cooled and extracted with 1 ml of diethyl ether so that practically the entire reaction product is transferred to the ether layer (if more ether becomes necessary for complete extraction, the extract should be concentrated to 1.0 ml by distillation. From the extract, 1 μl of solution was taken in a gas syringe and injected through a GC port. This is the general method for all the substrates used here. In the cases of solid substrates their solutions in acetonitrile were used. The reaction was monitored by GC every 1 h interval. Parr type apparatus is not absolutely necessary for the laboratory as well as industrial method for the oxidation

of these substrates, but in quantitative physico-chemical studies like reaction kinetics a very good and reproducible curve fittings are obtained if the experiment is done in a closed system and that is practicable in Parr type apparatus.

2.6. Isolation of the oxidized products and recovery of catalyst

Each of the reaction mixtures left after the catalytic oxidation was over, excepting where the product was pyridine N-oxide (PyNO), was thoroughly shaken with diethyl ether repeatedly when each of the substrates and the products and the CH_3CN solvent were almost quantitatively extracted in the ether layer. The ether layer was separated out and from the extract, substrate and products were separated by fractional distillation. In the case of pyridine as substrate the said reaction mixture was thoroughly and repeatedly shaken with CH_2Cl_2 in a seperatory funnel when both the Py and PyNO came to the CH_2Cl_2 layer. The CH_2Cl_2 and pyridine was then distilled out until a very small amount of liquid remains. The liquid on cooling (ice) deposits colorless shinning crystals of PyNO. The yellow-colored aqueous layer on spectral probe contains oxoperoxo vanadium complex with $PBHA^-$ as shown in Section 3.5. The solution was treated with a little ethanol solution of PBHAH and 2–3 drops of concentrated HCl when the color changed to purple and a purple solid was separated out, filtered off, washed and dried. This purple product was identified by its IR spectrum which was

superimposable with that of the (structurally characterized) compound, **1**.

3. Results and discussion

3.1. Catalytic oxidation

A scrutiny of the oxovanadium complex [V(O)(Cl)(PBHA)$_2$] **1** as catalyst with H$_2$O$_2$ as terminal oxidant reveals that **1** is a very efficient and highly selective catalyst and its efficiency towards hydrocarbon oxidation is more pronounced than the widely used oxovanadium catalyst [VO(acac)$_2$] (confirmed by parallel experiment done by us) which is otherwise very much effective for olefin epoxidation. It may be iterated that no optimization work in the form of addition of co-catalyst promoter or acidic or basic reagents and other additives sometimes necessary for hydrocarbon oxidation work [7(f)] does not show any change in the catalytic potentiality and so the results in Table 1 may be taken as an example of an exclusively substrate→oxidant→catalyst reaction which is self-optimized. Moreover, the control experiment does not show any noticeable oxidation. Hence, the hydrocarbon (aromatic, heterocyclic, carbocyclic and aliphatic, see Table 1) oxidation method reported here and the result achieved including the catalyst recovery method is an example of environmentally benign, cost-effective and highly potential catalytic oxidation process of hydrocarbon and superior to other such work especially in terms of selectiv-

ity and TON. Now, before formulating a reaction pathway and probable mechanism, the catalyst characterization work done is shown below.

3.2. General characterization, IR and spectral analysis

1 is non-electrolyte in acetonitrile as well as in nitromethane. It is diamagnetic, appropriate for a d^0 system and the violet color which gives rise to an absorption maximum in the visible region (see Section 2) is originated from PBHA→VO^{3+} LMCT transition. The two shoulders, which appear in the UV region, are due to intra-ligand transitions. In uncoordinated PBHAH the ν (C=O), ν (N–O) and ν (C–N) vibrations appear as strong bands at 1630, 925 and 1470 cm^{-1}, respectively [21]. After complexation with oxo-vanadium(V), ν (C=O) undergoes a strong negative shift and appear at 1530 (s) and 1500 (s) cm^{-1} due to the creation of two strong V–O (PBHA) bonds, one being slightly longer than the other (see Fig. 1 and the captions to the figure for the relevant bond lengths). The negative shift is due to a drainage of electron density from carbonyl oxygen to vanadium which in its turn weakens the O→C dative π bonding and hence the C–O bond order is lowered. The minor change of the ν (N–O) vibration after coordination (920 cm^{-1} for **1**), is due to two inductive effects operating at cross purposes, one is the weakening of the N–O bond due to the weaker O→N π overlap after O-coordination. Again, this O-coordination causes remarkable increase in the electronegativity of N atom, which then attracts electron density from the aromatic ring. The ν (C–N) vibration
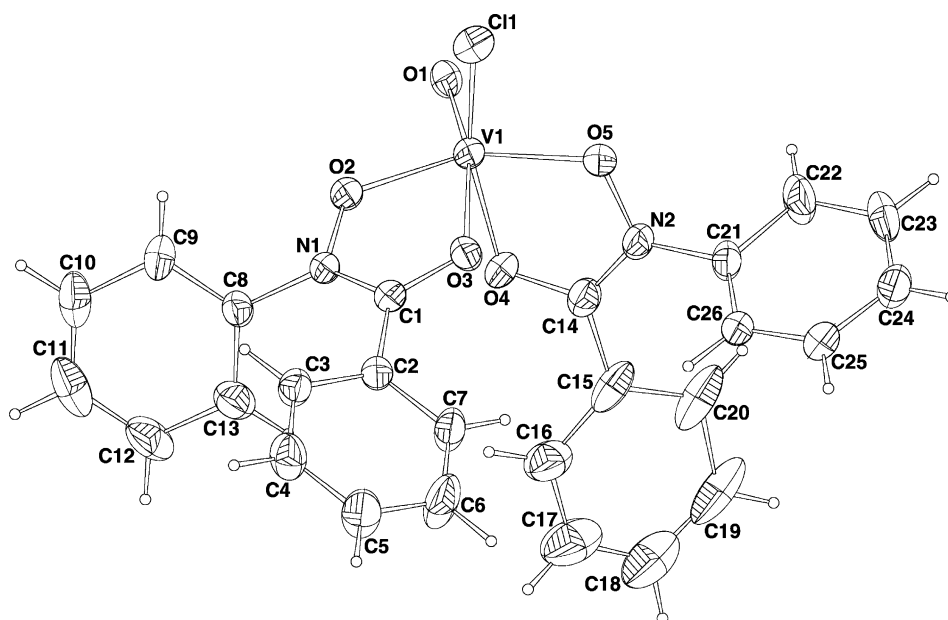

Fig. 1. ORTEP view of [V(O)(Cl)(BPHA)$_2$] (**1**) with selected bond distances (Å) and angles (°): V1-O1, 1.801(3); V1-O2, 1.875(3); V1-O3, 2.153(3); V1-O4, 2.043(3), V1-O5, 1.911(3); V1-Cl1, 2.166(18); C1-O3, 1.264(5); C14-O4, 1.275(5); N1-O2, 1.362(4); N2-O5, 1.358(5); N1-C1, 1.326(5); N2-C14, 1.324(7); O1-V1-Cl1, 95.88(11); O1-V1-O2, 91.80(13); O1-V1-O3, 167.07(12); O1-V1-O4, 98.30(14); O1-V1-O5, 106.72(14); O2-V1-O3, 75.47(12); O2-V1-O4, 88.39(13); O2-V1-O5, 157.72(13); O2-V1-Cl1, 103.87(12); O3-V1-O4, 79.43(13); O3-V1-O5, 85.29(13); O4-V1-O5, 76.96(14); Cl1-V1-O3, 89.44(10); Cl1-V1-O4, 160.93(10); Cl1-V1-O5, 86.81(13).

occurs as two strong bands at 1455 and 1445 cm^{-1} showing that change in C–N bond order after coordination is marginal. This 10 cm^{-1} change in the position of the two C–N vibration is also reflected in the inequality between the two C–N bond lengths. The ν (V=O) vibration occurs as a strong band at 970 cm^{-1} [22] and the ν (M–Cl) vibration appears at 360 cm^{-1} which is a bit higher than the expected region for the said vibration [23]. Notably the pure PBHAH is transparent in this region.

3.3. Molecular structure

In the complex **1**, an oxo, a chloro group and two bidentate hydroxamate ligands in cissoids configuration surround the vanadium atom. The coordination environment around the V center can be best described as distorted octahedral with O2, O4, O5 and Cl1 atoms defining the equatorial plane with O1 and O3 atoms occupying the axial sites; the V1 atom is displaced by 0.263(2) Å from the least-squares plane towards the oxo (O1) ligand. The degree of distortion in the metal coordination geometry is reflected in the large variation of metal-donor atom bond distances [1.801(3)–2.166(2) Å], small bite angles of the chelate rings [75.5(1)°–77.0(1)°] and dissimilar trans angles of 157.7(1)°, 160.4(1)° and 167.1(1)°. The oxovanadium bond length V1–O1 [1.801(3) Å] is longer than V=O distances reported in the literature [24,25]. As expected, the axial V1–O3 bond length [2.153(3) Å] is elongated compared to the V–O (equatorial) distances lying in the range 1.875(3)–2.043(3) Å. The V1–O3 length is, however, significantly shorter than 2.242(2) Å, the V–O distance trans to the oxo-metal bond observed in octahedral oxo-vanadium(V)-hydroxamate complex [24] in a mixed ligand environment. The observed deviation in V=O and V–O (axial) bond lengths are presumably due to co-planarity

Fig. 3. Percentage yield vs. time (h) plot for the conversion of toluene to benzaldehyde (i), benzene to phenol (ii), cyclohexane to cyclohexanol (iv) and cyclohexanone (iii) using **1** as catalyst. For the above kinetics measurement, substrate:catalyst = 800:1.

of O1, V1, O3, C1 and N1 atoms resulting in the possibility of extended π-conjugation in this part of the molecule. Similarly the coplanarity of Cl1, V1, O4, C14 and N2 atoms influences the V1–Cl1 bond distance and the observed value 2.166(2) Å is shorter than 2.308(1) Å reported for octahedral chloro-vanadium(V) complex [26]. Consistent with these is the average C=O distance 1.270(5) Å, which is longer than the values 1.20(2)–1.25(1) Å for free hydroxamic acid [27]. The five-membered vanadium-hydroxamate chelate rings are nearly planar and inclined to each other by 72.5(1)°. Due to steric constraints the phenyl rings are twisted with respect to the hydroxamate groups by 35.2(2)°, 33.8(3)° about the C–C bond and 61.4(1)°, 67.2(2)° about the N–C
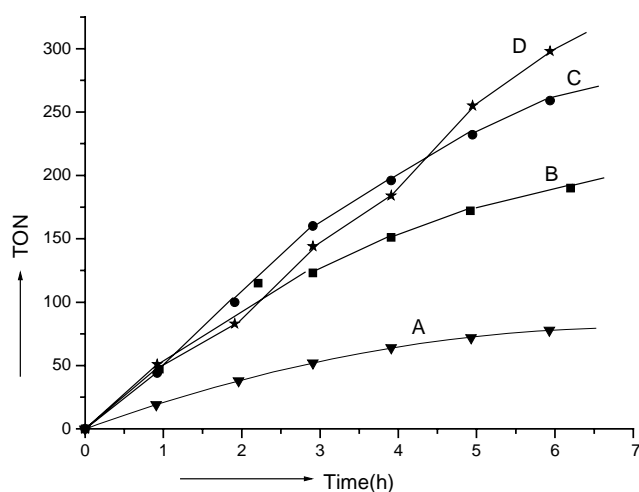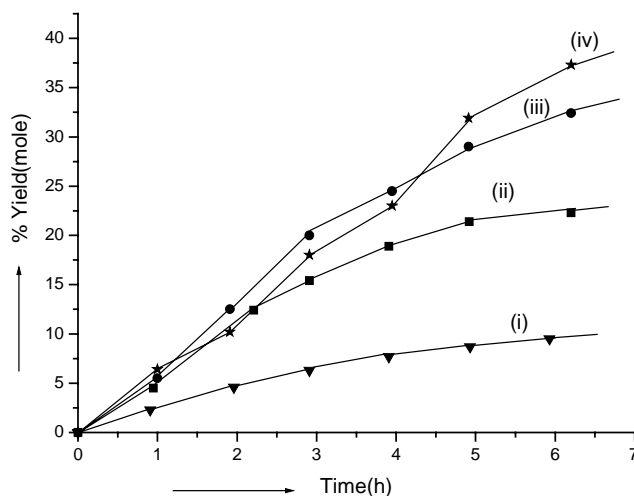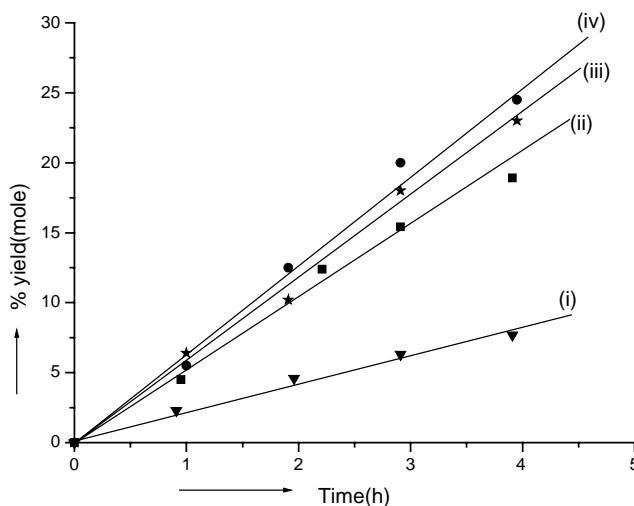

Fig. 2. Turnover number TON vs. time (h) plot for the conversion of toluene to benzaldehyde (A), benzene to phenol (B), cyclohexane to cyclohexanol (D) and cyclohexanone (C) using **1** as catalyst. For the above kinetics measurement, substrate:catalyst = 800:1.
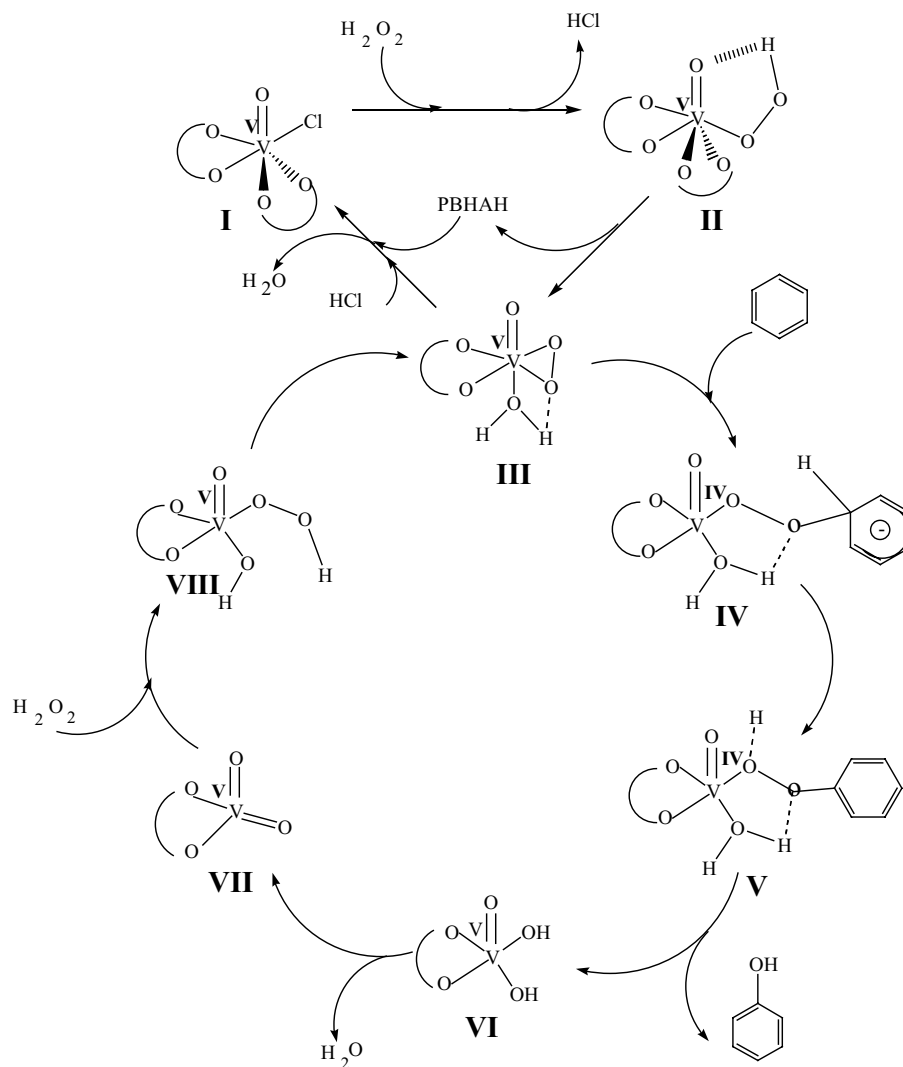

Fig. 4. K_{obs} for toluene to benzaldehyde (i) = 2.11 mol h^{-1}, that for benzene to phenol (ii) = 5.2 mol h^{-1}, and the same for cyclohexane to cyclohexanol (iii) = 6.30 mol h^{-1} and for cyclohexane to cyclohexanone (iv) = 6.32 mol h^{-1}.

Scheme 1.

bond. In the crystal packing of complex (1), the atom C6 at (*x*, *y*, *z*) is hydrogen bonded via H6 to O5 at ($-x + 1$, $y + 1/2$, $-z + (1/2) + 1$) forming infinite molecular chains along the [1 0 1] direction of 1.

3.4. Time dependence of hydrocarbon oxidation

A plot of time (in h) versus TON (Fig. 2) as well as yield percentage (Fig. 3) for three representative substrates viz. toluene, benzene and cyclohexane indicates that the oxidation starts right from the beginning and then the conversion rate goes on increasing linearly until 4 h (Fig. 4). After 4–4.5 h the rate becomes slower. Best straight lines are drawn from the five earlier points taking origin as point 1 (Fig. 4), and from the slopes of the respective straight lines K_{obs} for toluene to benzaldehyde (i) = 2.11 mol h^{-1}, that for benzene to phenol (ii) = 5.2 mol h^{-1}, and the same for cyclohexane to cyclohexanol (iii) = 6.30 mol h^{-1} and for cyclohexane to cyclohexanone (iv) = 6.32 mol h^{-1}.

3.5. Probable reaction pathway and mechanistic aspect

The mechanism of the reaction is not fully clear. However, insensitivity of the catalytic reaction towards AIBN and benzoquinone leads us to assume a non-radical mechanism. So the sequence of reaction steps is framed as shown in Scheme 1. During catalyst recovery experiment (see Section 2.6) PBHAH was extracted in ether but not the oxoperoxo complex **IV**. Hence to generate the catalyst from the aqueous layer extra PBHAH had to be added, proving thereby that the mechanism presented here is realistic.

4. Concluding remarks

V$_2$O$_5$ and the allied vanadium compounds were long known to have industrial uses as substrate oxidation catalyst operating in heterogeneous mode. But solid vanadium compounds act as irritants to the conjunctive and respira-

tory tract. Consequently the inhalation of catalyst dust is extremely unpleasant and should be avoided [28]. In this respect, this work on the development of homogeneous hydrocarbon oxidation method employing a suitable oxovanadium(V) catalyst operating under environment friendly condition with good yield percentage and TON and a smooth catalyst recovery technique should be considered to be a very useful methodology. The preliminary results obtained from a kinetic run show that the speed of the reaction is also good but the details of the kinetic work is presently left out, as it is not necessary at this point.

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